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The algebraic approach to the structure and dynamics of molecules has been applied in a number of ways:

- The ability to compute the spectra of energy-rich molecules has been demonstrated.
- Broad gateway states have been examined for vibrationally excited molecules.
- A link between the intramolecular dynamics and the statistical analysis of spectra has been established.
- The underlying potential energy has been determined directly from the observed spectra.
- The intramolecular dynamics of vibrationally excited acetylene has been studied and the spectral signatures of vibrational energy pathways have been examined.

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PUBLICATIONS

"Molecular Reaction Dynamics and Chemical Reactivity", R D Levine and R B Bernstein, Oxford University Press (1987)

"The Theory and Practice of the Maximum Entropy Formalism", R D Levine, *in* Maximum Entropy in Applied Statistics, J.H. Justice, ed. (Cambridge Univ. Press, Cambridge, 1986)

"Anharmonic Local Mode - Normal Mode Transformations: An Algebraic Treatment", R D Levine and J L Kinsey, *J Phys Chem* **90**, 3653 (1986)

"Transition Strength Fluctuations and the Onset of Chaotic Motion", Y Alhassid and R D Levine, *Phys Rev Lett* **57**, 2879 (1986)

"The Square Well Potential by an Algebraic Approach", S Kais and R D Levine, *Phys Rev A* **34**, 4615 (1986)

"Tunneling and Dynamic Tunneling by an Algebraic Approach", R D Levine, *in* Tunneling, J. Jortner and B. Pullman, eds. Reidel, Dordrecht 1986, p. 1.

"The Distribution of Intensities in a Vibrational Spectrum: A Computational Study", J Brickmann, Y M Engel and R D Levine, *Chem Phys Letters*, **137**, 441 (1987)

"An Algebraic Approach to Collision Dynamics of Composite Projectiles", M Berman and R D Levine, Proc. 1986 Group Theory in Physics Conference Invited Lectures, *in* XV International Colloquium on Group Theoretical Methods in Physics, R. Gilmore ed., World Scientific 1987, p. 336

"Algebraic Approach to Molecular Spectra and Dynamics", R D Levine, *in* XV International Colloquium on Group Theoretical Methods in Physics, R. Gilmore, ed., World Scientific Publishing Co., 1987 p. 28

"Quantal Fluctuations in Fluorescence Lifetimes of Individual Rovibronic Levels", Y M Engel, R D Levine, J W Thoman, Jr., J I Steinfeld and R McKay, *J. Chem Phys,* **86**, 6561 (1987)

"Fluctuations in Spectral Intensities and Transitions Rates", R D Levine, *Adv Chem Phys* **70**, 53 (1987)

"Quantal Equations of Motion for Information-Theoretic Constraints: Numerical Results for the Landau-Teller Potential", M Berman and R D Levine

"On the Group Theoretical Formulation for the Time Evolution of Stochastic Processes", R D Levine and C E Wulfman, *Physica,* **141A**, 489 (1987)

"Directed States of Molecules", S Kais and R D Levine, *J Phys Chem,* **91**, 5462 (1987)

"Comment on the High Stretch of Water", I Benjamin and R D Levine, *J Mol Spectr* **126**, 486 (1987)

"Intensity Fluctuations in Quantal Spectra as a Measure of Diffusion in Phase Space", J G Leopold and R D Levine, *Europhys Lett* **6**, 291 (1988)

"Quantal Fluctuations in Spectra", R D Levine, *in* Large Finite Systems, J. Jortner and B. Pullman, eds., Reidel, Boston, 1987

"Lie Algebraic Approach to Molecular Structure and Dynamics", R D Levine, *in* Computational Physics and Chemistry, Springer, New York 1988, p. 242

"The Analysis of Intensity Fluctuations for a Fully Resolved Spectrum, Pyrazine", J Kommandeur, Y M Engel and R D Levine, *J Chem Phys* **88**, 6810 (1988)

"Fluctuations in Intensities of Stimulated Emission of Acetylene: An Example of the Simplectic Ensemble?", J P Pique, R D Levine and J L Kinsey,

"An Algebraic Hamiltonian for Electronic and Nuclear Degrees of Freedom Based on the Vector Model", T A Holme and R D Levine, *Int'l J Quant Chem* **34**, 457 (1988)

"Quantal Fluctuations in Unimolecular Rate Constants", R D Levine, *Ber. Bunsenges Phys Chem* **92**, 222 (1988).

"Chemical Reaction Dynamics - The Study of Molecular Reactivity and Disequilibrium", R D Levine, *Bull Chem Soc Japan,* **61**, 29 (1988)

"Information Theoretic Analysis of Quantal Fluctuations in Fluorescence Lifetimes", Y M Engel, R D Levine, J W Thoman, Jr., J I Steinfeld and R McKay, *J Phys Chem* **92**, 5497 (1988)

"Gateways in the Stimulated Emission Pumping Spectrum of Acetylene", J P Pique, Y M Engel, R D Levine, Y Chen, R W Field and J L Kinsey, *J Chem Phys* **88**, 5972 (1988)

"Bond Selective Processes in Laser Desorption Studies as an Example of Inefficient IVR Mediated by Low Frequency Modes", T A Holme and R D Levine, *J Chem Soc Faraday Trans*. II **84**, 1630 (1988)

"Intensity Distribution in Rotational Line Spectra: II. Analysis of the Fluctuations in the Doppler-free $S_1 \rightarrow S_0$ Spectrum of Benzene", Y M Engel and R D Levine, *J Chem Phys* **89**, 4633 (1988)

"A Measure of Chaos in Quantum Algebraic Systems", F Iachello and R D Levine, *Europhys Lett* **4**, 389 (1987)

"The Statistical Wavefunction", R D Levine, *J Stat Phys* **52**, 1203 (1988)

"Short-Time Vibrational Dynamics of Acetylene *vs*. Its Isotopic Variants", T A Holme and R D Levine, *Chem Phys Lett* **150**, 393 (1988)

"Theoretical and Computational Studies of Highly Vibrationally Excited Acetylene", T A Holme and R D Levine, *Chem Phys*

"Intramolecular Dynamics", R D Levine, Invited Lectures, 6'th International Congress of Quantum Chemistry, Jerusalem 1988

"Construction of Triatomic Potentials from Algebraic Hamiltonians Which Represent Stretching Vibrational Overtones", I L Cooper and R D Levine,

"Computational Studies of Rapid Laser Induced Desorption: A Microscopic Mechanism for Selectivity", T A Holme and R D Levine, *Surf Sci*

"Proposed Cooperative Model of Dissociative Chemisorption", I Oppenheim and R D Levine, *Chem Phys Lett*

"Dimensional Scaling by an Algebraic Approach", S Kais, D R Herschbach and R D Levine (in preparation)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The spectrum and dynamics of polyatomic molecules have been studied in the higher energy range. The algebraic approach has been shown useful even in the rage of very high overtones. Realistic potential energy surfaces, valid all the way to dissociation, could thereby be constructed from observed spectra. Even when the simpler algebraic Hamiltonians, which do possess some symmetry, no longer fully suffice, it was found that the symmetries still account for the coarse features in the spectra. Classically, these features can be associated with unstable orbits which do however have short term stability. At higher resolution the spectral intensities show fluctuations about their smooth envelope. Contrary to naive expectations, these do not die out even when all selection rules have broken down. Analysis of these fluctuations has been proposed on theoretical grounds, validated against several computationa studies and applied extensively to experimental data.

The analysis of spectra on the one hand and computational studies on the other, have revealed that many realistic polyatomic systems exhibit a clear 'separation of time scales' in their dynamics. Within each time regime a particular subset of states is strongly coupled. Within that subset, the energy exchange is RRK-like involving frequent exchanges of small amounts of energy. In classical phase space, the motion is diffusive-like. The different subsets, which correspond to distinct values for algebraic symmetry operators, are essentially uncoupled. The transition from one time domain to the next is evidenced by an abrupt impulsive exchange of energy amongst previously non-interacting subsets of states. It appears from our results that the necessary condition for such behavior is a spread in the characteristic frequencies so that, in the language of non-linear mechanics, the system can exhibit a sequence of resonances of increasing order. The time for dominant coupling of most states can be, for realistic systems, many hundreds of vibrational periods giving rise to the possibility of experimental selectivity.

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ENERGY AND CHEMICAL CHANGE

COMPREHENSIVE FINAL REPORT

submitted to

Air Force Office of Scientific Research

by

James L. Kinsey

and

Raphael D. Levine

November 1988

Contents

1. Scientific Progress Report

We have proposed a study of spectra and dynamics of energy rich molecules using an algebraic approach. Our activities have followed the different specific directions as discussed in the original proposal. Papers which have been published or submitted are listed in section 3. In particular we mention the highly anharmonic square well potential for which a simple algebraic description was provided [4], the applications to tunneling [5], a series of papers on spectral fluctuations (review, [10]), a paper [13] on algebraic aspects of oriented molecules which is relevant to steric effects in chemical reactions, the elucidation of vibrational energy pathways of highly excited acetylene, ([19, 24, 25, 29-31]; see appendix), and the construction of realistic potential energy surfaces from observed spectra. Late in 1987 Oxford University Press published 'Molecular Reaction Dynamics and Chemical Reactivity' by R.D. Levine and R.B. Bernstein. The preface records our primary indebtedness to the Air Force Office of Scientific Research.

The highlights of the first project year were two new starts both of which look like they will keep us busy for some time to come. The first is an unexpected outcome of our ability, due to the algebraic approach, to compute spectra of energy rich molecules. Such computed spectra show a wide variation in transition intensities, quite reminiscent of the spectra measured, e.g. by Kinsey and Field, using stimulated emission pumping to high lying final states. The possible interpretation [3] was presented at the October 1986 contractors meeting. Following discussion there with Steinfeld, it became clear that the same interpretation would hold for the rapid variation in fluorescence rates observed in SiH_2 [9,23]. More work has been done almost immediately [6,10] and an invited review has been published in Advances in Chemical Physics. Since these original studies, we have incorporated such additional aspects as thermal averaging for the initial state. Furthermore, an explicit link between the intramolecular dynamics and the statistical analysis of the spectra has been established [15]. The resulting development opens up the possibility of approximate but practical computation of spectra for polyatomic molecules. During the second and third project years we have also considered additional experimental examples, e.g. [18,26]. Foremost amongst those have been the stimulated emission pumping results on acetylene which have stimulated the entire approach. In close cooperation with Dr. Pique who measured the spectra in the laboratory of Professors Kinsey and Field, the fluctuations were analyzed [19]. It was concluded that four independent components contribute to the transition amplitude. Earlier work on spectral rigidity by Pique, Kinsey and coworkers was also re-examined leading to a similar conclusion (3-6 components). Using an averaging procedure to produce a low resolution spectra, these components were tentatively identified as giant gateway states [24]. It was conjectured that these are primarily trans-bend vibrational states as expected for a dump transition onto a linear ground state from an excited state whose equilibrium geometry is trans-bent. During much of the third project year we worked on detailed studies of the spectral implications of the intramolecular dynamics of acetylene. Our current results suggest that the original conjecture was wrong. For the initial conditions selected by stimulated emission pumping, it is the relatively unexcited CH stretch modes that are the first to respond. It is this short time dynamics that appears to correspond to the broad spectral features. The current thinking about acetylene as well as some generalizations about intramolecular dynamics is provided in the appendix. It is argued therein that in many realistic systems the spread in values of the vibrational frequencies is such that statistical (or RRK-like) behavior does not occur before many hundreds of vibrational periods. Also the mechanism of IVR appears to be non-RRK like. Rather, long intervals of very regular behavior are punctured by brief impulsive exchange of large amounts of vibrational energy. These characteristics and the detailed studies giving rise to these conclusions are reviewed in the appendix. We regard this demonstration of non-statistical dynamics in realistic systems over time scales where experimental probing is readily feasible, as the important result of the third project year.

The second significant new development of the first project year was planned but is all the same pleasing. The method of surprisal synthesis has been fully implemented for computor computations [5,9]. We have worked so hard and for quite a while on this problem that in the end very much of the work is analytic. For example, for vibrational energy transfer we need a numerical effort equivalent to computing a *single* classical trajectory in order to determine the surprisal parameters directly from the Hamiltonian. The method is fully quantal and the computational effort does not increase with increasing energy. Indeed our 'problem' is that conventional fully quantal computations are typically prohibitive over much of the chemical range and we have no benchmarks against which to compare the results.

In the second project year we also have initiated the proposed study of algebraic potential energy surfaces which contain a barrier. The initial approach which generated surfaces at the LEPS (London-Eyring-Polanyi-Sato) and DIM (Diatomics In Molecules) levels of accuracy is completed [20]. We have also returned to the algebraic description of bent molecules and are now fully in a position to generate potential energy surfaces, not only for the stretch but also for the bending motion. This means that we can determine the parameters in the algebraic Hamiltonian from the observed spectra and then derive the corresponding potential. This provides an inversion procedure of considerable promise since the potentials we obtained for the stretch motions were remarkably accurate and realistic. In any case, there is no other strict inversion procedure.

2. Ongoing Activities

Specific points arising out of this project and which are being actively worked on include:

(a) The computational study of the intramolecular dynamics of highly excited acetylene is being continued. The purpose is to firm the identification of the broad gateway states and the implications for the temporal evolution, see appendix. The second aim is to see if similar states can be expected in other systems as well and how far they can be accessed via other means of excitation.

(b) New applications of the algebraic description of spectra with special emphasis on recent measurements for HCN and CO_2. For HCN we are computing the intensities in a purely algebraic way. The purpose here is two-fold. The first is to compare with the recent measurements for high overtones by Prof. W. Klemperer. The second is to fully validate the algebraic Hamiltonian in anticipation of the planned SEP experiment by Prof. R.W. Field. For SO_2, the recent very extensive set of levels assigned in the SEP experiment of Prof. Tsuchiya will be computed. Right now, SO_2 has more known overtones than any other molecule.

(c) Complete the study of fluctuations in spectral intensities and transition rates. Here we expect to (i) Analyze more data and (ii) Improve the link with the Hamiltonian of the system. A start in that direction was already made [15] but much more work is required. Eventually, we hope to generate not just spectral positions but also intensities using the *minimal* set of relevant observables.

(d) The further development of an algebraic approach to potential energy surfaces for systems which contain a barrier as is typical for direct molecular reactions and the applications of the method (which now includes the bending coordinate) to 'inversion' of spectra, [33] with special reference to H_2O, O_3, HCN and the van der Waals molecules Ne·HCl and Ar·HCl.

Papers submitted for publication under Grant AFOSR 86-0011:

1. R.D. Levine, The Theory and Practice of the Maximum Entropy Formalism, *in* Maximum Entropy in Applied Statistics, J.H. Justice, ed. (Cambridge Univ. Press, Cambridge, 1986).
2. R.D. Levine and J.L. Kinsey, Anharmonic Local Mode - Normal Mode Transformations: An Algebraic Treatment, *J. Phys. Chem.* **90**, 3653 (1986).
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27. F. Iachello and R.D. Levine, A Measure of Chaos in Quantum Algebraic Systems, *Europhys. Lett.* **4**, 389 (1987).

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34. T.A. Holme and R.D. Levine, Computational Studies of Rapid Laser Induced Desorption: A Microscopic Mechanism for Selectivity, *Surf. Sci.*

35. I. Oppenheim and R.D. Levine, Proposed Cooperative Model of Dissociative Chemisorption, *Chem. Phys. Lett.*

36. S. Kais, D.R. Herschbach and R.D. Levine, Dimensional Scaling by an Algebraic Approach (in preparation).

INTRAMOLECULAR DYNAMICS

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ABSTRACT. There is currently both experimental and theoretical evidence that also in systems of many interacting atoms there can be dynamical selectivity with respect to initial mode of excitation and specificity with respect to final outcomes. This lecture provides a brief outline of the newly available results and examines in detail the dynamics of highly vibrationally excited acetylene.

1. Introduction

The conventional wisdom for intramolecular dynamics is that on time scales of chemical interest, highly excited states of polyatomic molecules behave statistically. In other words, there is enough time for the excess energy to be shared amongst all modes. The 'chemistry' of the molecule will then be governed only by its total energy rather than by any detail of its initial preparation. The earlier evidence in support of this point of view [1], provided mainly by chemical activation experiments [2], has more recently been augmented using activation via optical excitation and in particular multiple (infrared) photon absorption [3,4]. The purpose of this lecture is to go beyond this point of view. We point out that there is currently a wealth of evidence, for many different types of systems, that the conventional wisdom needs refinement. We then examine a particular example in some detail.

Lecture at the 6'th International Congress of Quantum Chemistry

2. Background

The need for reexamination of intramolecular dynamics is stimulated by the experimental progress which has resulted in both shorter times in which systems can be excited and/or probed and in systems where the inherent time scales for energy redistribution are longer than for ordinary polyatomic molecules. Starting with the latter, experiments are now possible on systems of many interacting atoms where the range of vibrational frequencies is far wider than is the case for polyatomic molecules made up from atoms of comparable mass. This is achieved in primarily two ways. The first is to have forces of qualitatively different strengths coupling the atoms in the system. An example is a van der Waals adduct of two molecules. The chemically bonded atoms interact much more strongly than those coupled by the (nominally, non-bonding) van der Waals forces. Clusters, molecules physisorbed on surfaces and chemical reactions in liquids are additional examples.

The intramolecular dynamics of systems of atoms which interact with forces of different scales is so rich that we discuss some examples in more detail in the next section.

The other way to introduce a significant frequency mismatch is by changes in the mass. (Of course, one can do both, as in a chemical reaction in solution where the reactants and solvent molecules have quite different masses). Even in chemical activation days, the C-H modes presented a problem and our example of acetylene is similar in that respect. An opposite extreme, also encountered first in chemical activation, is heavy atom blocking, [5].

The tighter preparation of the initial state and its probing can be achieved in either the time or the frequency domains. The experimental ability to observe the system during the chemical act and hence to monitor the dynamics in real time [6] has been widely acclaimed. It should however be emphasized that one can get equivalent information from the frequency response, whether it is the emitted fluorescence [7,8] or the absorption spectrum [9,10] of the system [1]. The work of Heller [11,12] on the equivalence of short time dynamics and coarse grained spectra (and *vice versa*) has contributed significantly to this point.

Since comparatively short propagation times are required to generate the major spectral features, there is a renaissance of time-dependent quantal computational methods. These include exact [13] and approximate [14,15] wave packet propagation, time-dependent self-consistent-field theories [16], path integral techniques [17], algebraic-based approaches [18] and RRGM-based methods [19]. New methods for the analysis of complex spectra, which go beyond the near neighbors spacing distribution [20], are also being developed [21-24].

Progress in non-linear dynamics has also had a significant impact. The importance of 'resonance' frequency match or lack thereof contributed to the development of local mode models [25-27]. Another central idea is that of Cantori [28,29] (closely related to vague tori [30] and to intermittency). This is the observation that when two modes of evolution are energetically accessible, the system will not necessarily smoothly change between the two. Rather, it will spend quite some time in one mode (as if it were the only allowed mode) and then make a rather sudden, impulsive transition to the other. The sudden onsets of new modes of motion will be quite evident in the example of acetylene, as discussed in detail below. It is because of this characteristic that we are able to delineate distinct stages in the temporal evolution of highly excited acetylene.

Furthermore, because these stages correspond to different time scales, they have their signature in the observed spectral features.

It is this separation of time scales with a corresponding (yet tentative) experimental identification via different levels of spectral resolution that make acetylene a particularly intersting test case. Other molecules whose intramolecular dynamics have been theoretically studied in detail include C_6H_6 [31-36], CH_2O [37,38] and H_3^+ [39-42]. So far, we have discussed the intramolecular dynamics on the ground electronic surface. There is, of course, a wealth of data and theory for the dynamics on the first electronically excited surface. We refer to recent reviews for more details [43,44].

3. Reactive Processes

Most of the systems mentioned so far were bound states. In this section we briefly review theoretical studies of reactive processes in many atom systems. In each case one can regard the collection of interacting atoms as a polyatomic molecule. Simple unimolecular rate theory will then suggest that any selective initial excitation will rapidly equilibrate. Yet all three classes of processes to be discussed exhibit distinct dynamical features.

3.1 VAN DER WAALS MOLECULES AND CLUSTERS

Deviations from the simple RRKM picture are to be expected for molecules where there is considerable frequency mismatch among the coupled coordinates [45]. This has been clearly demonstrated for van der Waals molecules [45-47] and, in particular for the $I_2 \cdot He$ complexes [47-51]. What is of particular interest here is the mechanism of dissociation. The trajectory simulations show that the motion in the van der Waals well is largely unperturbed (due to the poor resonance between its frequency and that of I_2) until a rare short range repulsive interaction between He and an I atom which delivers an impulse sufficient to dissociate the van der Waals bond. The important point is that the rate of dissociation is essentially the rate of energy transfer [52]. This is not found to be the case for van der Waals systems (e.g., Ar_3 [53] where the frequencies are commensurate, energy exchange is facile and the RRKM point of view is quantitatively useful [54]. Even for rare gas clusters [55,56] e.g., Br_2 in Ar and for collisions such as Xe + Ar_2 [57] one finds that impulsive collisions provide the mechanism for energy transfer and evaporation. A similar bottleneck is operative when a vibrationally excited physisorbed diatomic molecule, with enough internal excitation to break the van der Waals bond to the surface, desorbs [58].

3.2 SURFACE DESORPTION

The desorption from a heated surface [59,60] can be discussed from a transition state theory point of view. For the purpose of considering the competition between desorption and surface reaction [61,62] it is convenient to regard the adsorbed species and the solid together as a polyatomic molecule that comes to thermal equilibrium more rapidly than any reactive change. The observed preferential desorption at higher heating rates is then due to the desorption rate constant having both a higher pre-exponential factor and a higher activation energy. At low heating rates, the temperature of the polyatomic system rises slowly and surface reaction dominates. For a rapid rise in the temperature, the temperature becomes rapidly high enough that the higher pre-exponential factor makes the desorption rate faster. It has been suggested [63] that this 'equipartition' picture may fail for physisorbed molecules. The argument is a continuation of the one in section 3.1. There, due to frequency mismatch there is no facile energy transfer from the chemical to the van der Waals bond. Here, due to frequency mismatch, energy does not readily flow from the low frequency physisorption bond to the internal modes of the physisorbed species. The physisorption bond acts as a bottleneck to energy flow from the solid to the molecule. Some support for this notion is provided by experiments [64,65] that suggest that even large polyatomics tend to desorb internally rather cold upon laser induced heating of the surface. Classical molecular dynamics simulations of desorption of diatomics from rapidly heated clusters [66] also show that physisorbed diatomics are desorbed cold. Even more important, the simulations show that desorption follows immediately an impulsive energy transfer from a cluster atom. As a further check, classical simulations [67] for diatomics tightly bound to the cluster or for diatomics which themselves are weakly bound (so that their internal frequency is commensurate with that of the physisorption bond or of the cluster), behave in a much more RRKM-like fashion, for the same heating rates that lead to selective desorption in the previous case.

3.3 REACTIONS IN LIQUIDS

Molecular dynamics simulations have been performed for a $Cl + Cl_2 \rightarrow Cl_2 + Cl$-like reaction with a 20 kcal/mol^{-1} barrier weakly coupled to a rare gas solvent, [68,69]. Examination of the trajectories shows that those that cross the barrier to reaction have acquired most of the energy necessary to do so via an impulse delivered primarily along the $Cl - Cl_2$ relative motion in the last 200 fs before reaching the barrier top. At 600 fs before reaching the barrier top and at earlier times, the energy distribution and the correlation functions are essentially those of thermalized reagents and solvent. Reaction requires an impulse delivered at the right time and in the right direction. This picture is different from an RRKM-like view of rapid energy exchange among many degrees of freedom (comprising the Cl_3 system and its environment). The motion toward the top of the barrier is not diffusive-like with many small kicks by the solvent to steer the reagents along. The relevant time scale (-200 fs) is such that only a single dominant impulse is delivered.

The second example is an S_N–2-like reaction in water solvent. The simulation [70] is for a $Cl^- + MeCl \rightarrow ClMe + Cl^-$ reaction where Me is a 'methyl atom' of mass 15 and the coupling to the polar water-like solvent by the ionic and dipolar reagents is strong. Given the potential surface and the results of preliminary simulations [71], it appears that vibrational energy in the reactant MeCl bond is needed in both the gas and aqueous phases in order to surmount the barrier. This can be understood by examination of the $(Cl\text{-}Me\text{-}Cl)^-$ potential energy surface, in the absence of solvent, as used in the simulation. The entrance valley runs very parallel to the Cl^--(MeCl) vector with practically no stretch of the MeCl bond. This entrance valley has a well and it ends up in a steeply repulsive wall. In the gas phase, reagents which are not vibrationally excited would come in and rebound from the wall. In the liquid some such trajectories can be trapped in the entrance valley. To follow the very sharp bend in the raction path which leads to the barrier, vibrational excitation is essential. (Just imagine rolling a ball [1] on the potential energy surface shown in figure 1 of [70]. $\beta = 45^\circ$).

4. Vibrational Energy Pathways in Acetylene

Highly vibrationally excited acetylene, in its ground electronic state can be prepared [72] in a two photon resonant process via the electronically excited $\tilde{A}$ state as an intermediate. (This is 'Stimulated Emission Pumping' or SEP, [73]. This double resonance technique results in an essentially purely vibrational spectrum and so eliminates rotational congestion). The equilibrium geometry of the intermediate state is trans-bent. The $C \equiv C$ bond is extended by about 15% as compared to the ground state, while the C-H bond length is hardly changed. At high resolution the spectrum is very dense, with a density of lines roughly comparably to the density of vibrational states that can be accessed. At a somewhat lower resolution the spectrum consists of 'clumps'. At *ca.* 26400 cm^{-1} of excess vibrational energy the density of clumps is about $0.6/cm^{-1}$, [22]. The high density of clumps suggests that they correspond to states with high trans-bend (the ν_4 normal mode) excitation. Since the intermediate $\tilde{A}$ state in the SEP scheme is trans-bent, it is possible that the clumps are the 'bright states' that carry oscillator strength. Our theoretical results do not support this interpretation but this conclusion is quite sensitive to our assumed potential energy surface.

The direct experimental observations establish therefore that there is an intermediate time scale in the problem, corresponding to the clump structure. Taking the Fourier transform of the high resolution spectra establishes [22] that this time is *ca.* 10 ps, corresponding to eigenstates interaction over a range of 3 cm^{-1}. One can also take the Fourier transform of the clump spectrum. The results are unexpected in that there is clear evidence for a short time process of *ca.* 0.5 ps. This corresponds to eigenstates interacting over a range of *ca.* 60 cm^{-1}. There is, therefore, a broad structure in the spectrum which can be clearly discerned upon coarse graining of the experimental frequency spectrum [74]. These broad spectral features, spaced about 200 cm^{-1} apart, are then the primary bright states.

4.1 TRAJECTORY COMPUTATIONS FOR HCCH

An empirical yet realistic potential energy surface was constructed [75] for acetylene in its ground electronic state. A harmonic approximation was used to generate the surface for the excited $\tilde{A}$ state. The 'classical' region on the ground surface which is accessed via SEP was defined as all the points on the lower surface where the potential energy difference to the allowed region on the $\tilde{A}$ surface equals the frequency of the transition. We [75] have chosen a transition corresponding to an excess vibrational energy of 26400 cm^{-1}. An ensemble of classical trajectories corresponding to different initial conditions in the classical region were computed. While these trajectories differed in their detailed time evolution, they mostly were similar in their overall behavior. This was not the case for other trajectories, computed at the same total energy but for quite different initial conditions.

Hence, while most trajectories eventually (i.e., for times longer than *ca.* 15 ps) become chaotic, the route to chaos does depend on the manner of the initial excitation. Even for a tetraatomic molecule at a very high level of excitation, the onset of chaos is not a simple process. This does however mean that our results will be somewhat sensitive to the assumption that the downward transition to the ground state is vertical and classically allowed. This caveat is important and must be borne in mind.

4.2 THE STRETCH MODES

The first modes to respond to the excitation are the two high frequency CH stretches. For over 0.5 ps (several tens of vibrational periods) these are the only modes that are coupled. The other three vibrational modes evolve independently of one another and of the CH stretches, [76].

From the very beginning of local mode models, it was proposed that the two CH modes are coupled via a resonant one quantum exchange [25,26]. It follows that the total number of CH stretch quanta will be conserved. The algebraic approach [77] clearly identifies the corresponding quantum number, denoted by *P*. States of given *P* lie in a band (a, so called, multiplet) which is well separated in energy from other multiplets of lower or higher values of *P*.

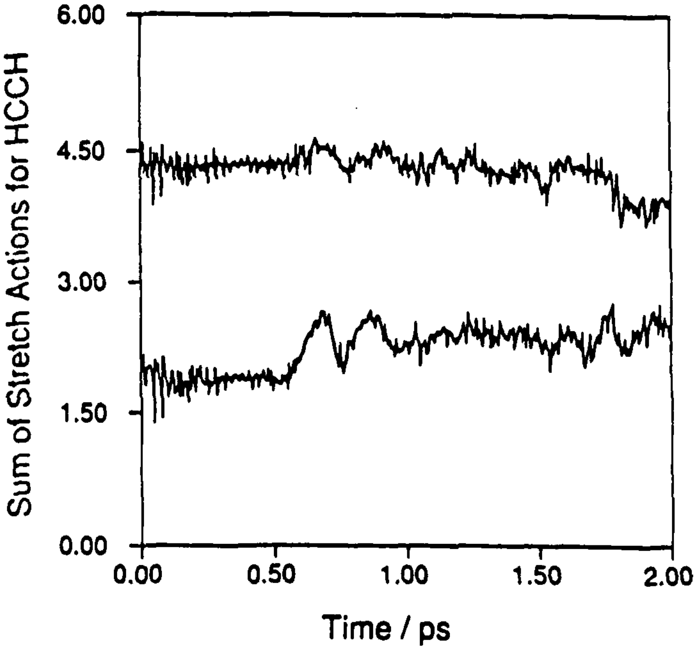

Figure 1. The sum of the classical actions in the two CH modes and in all three stretch modes vs. time. The classical actions are the analogues of the vibrational quantum numbers. Note that in the trajectory computations, the classical *P* is conserved for over 0.5 ps. Adapted from [78].

The C ≡ C bond is somewhat off-resonance with respect to the C-H stretches. Furthermore, due to the considerably long elongation in the $\tilde{A}$ state, it is initially highly excited and hence down shifted in frequency. Eventually, it does however couple to the CH stretches via a 1:1 resonance exchange. Then, it is only the sum of the quanta in all three stretch modes, figure 1, which will be conserved.

For DCCD, the C-D stretch frequency is significantly lower hence the coupling to the C ≡ C stretch will be that much more efficient. Indeed, the classical simulations show [78] that while the sum of the C-D stretch actions by itself is not conserved, the sum for all three stretch modes, is. Figure 2 shows the results.

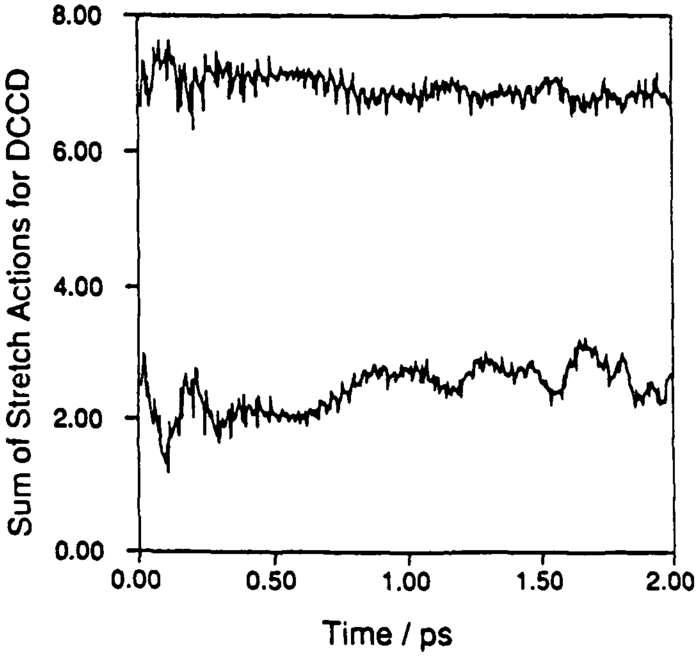

Figure 2. As in figure 1, but for DCCD the lower trace is the classical value of P.

Not so evident in figures 1 and 2 is the impulsive nature of the coupling. Hence figure 3 shows the energy in the C ≡ C bond vs. time. Particularly violent are the transfers to the bend past 2.5 ps.

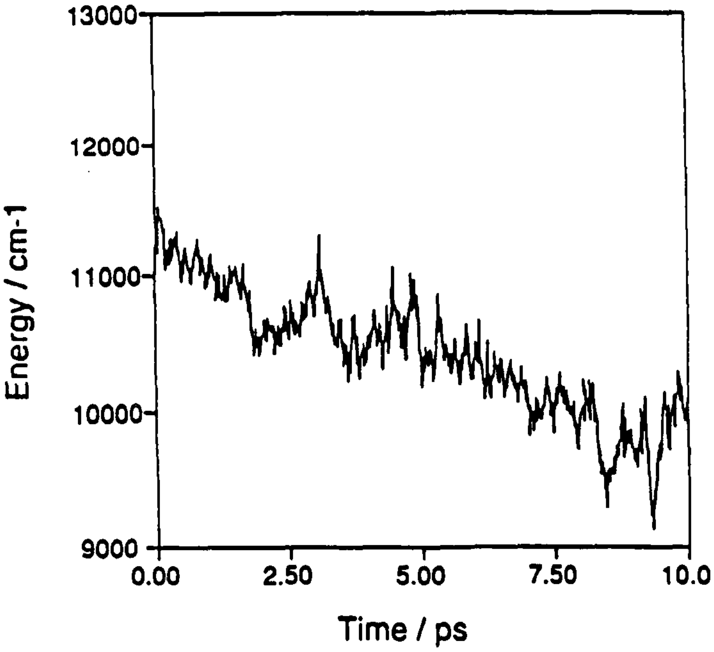

Figure 3. The vibrational energy in the $C \equiv C$ stretch of HCCH vs. time. Note the high initial value.

It should be reiterated that the conclusion that the CH stretch modes are the first to respond, very much depends on most of the initial conditions in our ensemble corresponding to finite initial excitation, say $P \sim 2$, of these modes. For trajectories corresponding to $P \sim 0$, the CH's remain decoupled from the $C \equiv C$ mode for much longer and the earliest coupling is that of the $C \equiv C$ stretch to the bends. Such initial conditions result in a longer time span prior to energy dissipation. A dependence of the dynamics on the initial region sampled in phase space has also been seen in other classical trajectory simulations [79,80].

4.3 THE TRANS-BEND AND THE CLUMPS

For both HCCH and DCCD, the trans-bend excitation (the ν_4 mode, excited because of the geometry of the $\tilde{A}$ surface), does not couple with the other modes for over 3 ps. The sharp spikes in figure 3 beyond 3 ps are due to the onset of this coupling.

Ultimately, the bend is very highly excited and the 'terminal' state for most of the trajectories is for the two hydrogens to 'rotate' in a fairly correlated fashion about the $C \equiv C$ core. What has not been observed is any significant 'trapping' in a vinyledene-like configuration. (Note however that the energy is about 10 kcalmol^{-1} over the barrier height for the isomerization [81,82].

The coupling of the trans-bend to the stretches leads to a corresponding quantum number in the algebraic approach. We believe that this (approximately conserved) quantum number is the leading to the clump structure in the observed spectra. We also note that to the same level of approximation l_4 is also conserved.

4.4 VINYLEDENE AND THE ORBITING MOTION

Further dynamical details can be obtained by computing time correlation functions, [75]. Taking the Fourier transform one can generate the corresponding frequency spectra. Moreover, one can compute the correlation function only for a time-slice of the trajectory. In this fashion one can discern when certain frequencies contribute to the motion. There are two particularly interesting results that have been obtained in this way. The first is that past the initial coupling of the bend to the $C \equiv C$ stretch (which is the energy reservoir, cf. figure 3), the computed frequency spectrum shows a weak peak at a $C = C$ frequency. This is the signature of vinyledene. The area under the peak is however less than 10% of the area of the $C \equiv C$ peak. The second result is the nature of the broad frequency response extending from zero to about 10 cm^{-1} with a flat maximum at *ca.* 6 cm^{-1}. This peak is generated by the terminal stage of the motion and corresponds to the rotation of the two hydrogens about the $C \equiv C$ core.

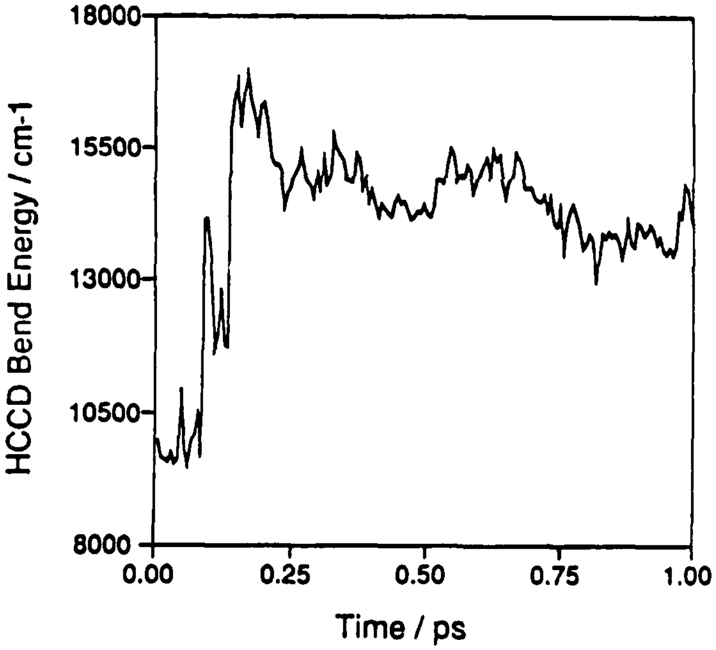

Figure 4. The HCCD bend excitation vs. time. Note the high initial value and its rapid increase.

4.5 HCCD

The computed dynamics for HCCD is quite different from the two symmetric isotopic variants, [78]. From very early on, the bends are strongly coupled to the stretches, figure 4.

The rapid increase in the energy of the HCCD bend is accompanied by a corresponding decline in the C ≡ C stretch excitation, figure 5.

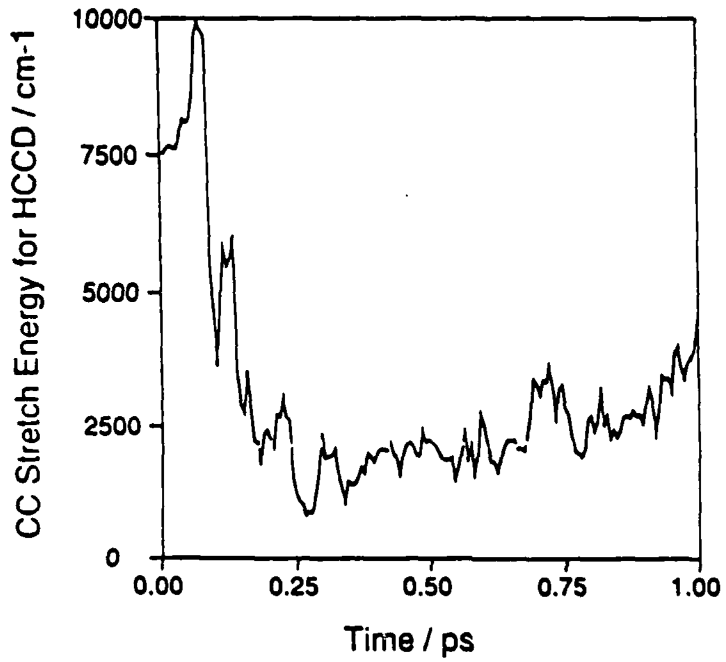

Figure 5. The C ≡ C stretch energy in HCCD vs. time. Ensemble average for the same set of trajectories used to generate figure 4. Note that the gain in energy shown in figure 4 is about compensated by the loss shown here.

The higher frequency C-X, X = H,D modes are about unperturbed during the initial rapid energy exchange between the bend and the C ≡ C stretch. It is only past *ca.* 2 ps that they are coupled to the other modes in a significant fashion.

The dynamical picture for HCCD has similarities with other systems where the large amplitude, soft, motions are the first to respond while the high frequency modes behave adiabatically. Since however all three molecules were computed using the same potential function it is not unreasonable to suggest that the broad and the intermediate spectral features for HCCD may be quite different than those of HCCH and DCCD. In particular, we note that it is possible for HCCH to show a behavior similar to HCCD if the initial conditions (at the same total energy) are drastically altered. It would therefore also be of interest to pump HCCH (or DCCD) via other intermediate states. In particular, the lower is the CH initial excitation (and the higher is the

$C \equiv C$ initial excitation), the more uncoupled are the CH stretches from the other degrees of freedom.

4.6 SUMMARY

The classical trajectory results show a hierarchy of sequential relaxation processes with fairly abrupt transitions from one regime to the next. The purely classical description is consistent with the set of approximate constants of the motion provided by the quantal algebraic approach. The separation of time scales is reflected in the frequency spectrum by features of distinct width, with the short time dynamics corresponding to the broadest features. Not yet subject to experimental test is the possibility that changes in the initial conditions can markedly affect the course of the relaxation nor the predicted isotope effects.

5. Concluding Remarks

Both experimentally and theoretically we are beginning to probe the very act of physical and chemical transformations. Even for systems consisting of many atoms there is now clear evidence that the temporal evolution following the initial excitation cannot be simply described as a rapid dissipation towards equilibrium. Rather, there is often a detailed pathway, with definite experimental signatures.

Very important for highly excited molecules are the large amplitude motions. It is therefore not sufficient to know the potential energy about some minimum energy path. For the case of acetylene, which was discussed in some detail, the theoretical interpretation of the observations for HCCH and the predictions for the isotopic variants are critically dependent on the potential energy function in the region accessed by the stimulated emission pumping and for large H-atom excursions.

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